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## THE EFFECT OF TRIPLET-TRIPLET EXCITATION ENERGY TRANSFER ON THE DNA SELF-PROTECTION MECHANISM

*The displacement of the DNA electronic energy levels, triplet electronic excitation energy transfer and their relation to the DNA damage under UV-irradiation were investigated by electronic absorption and phosphorescence studies. The lowest excited electronic triplet levels of the DNA (as well as the highest singlet levels) were shown to be related with adenine bases. However the AT-sequences are main traps for triplet excitation in the DNA and the DNA phosphorescence is connected namely with these traps. It was supposed that mobile triplet excitations in the DNA could spread on the distance of about 16 base pairs. According to the obtained results, main part of the triplet excitations in the DNA is finally localized on the photostable traps associated with AT-sequences. Thus, the hierarchy of the DNA bases electronic levels positions favors the triplet electronic excitation energy transfer process that leads to inhibition of photochemical destruction of the DNA. It was shown by the investigation of the DNA and base model compounds photodamage induced by UV-irradiation. The latter proves the existence of the DNA self-protection mechanism against damage of p-electronic systems of this macromolecule (caused by their excitations of different origins).*

**Keywords:** phosphorescence, fluorescence, triplet electronic excitation energy transfer, nucleotides, the DNA.

### Introduction

The electronic states of the DNA have been studied since early 1960–70s [1–10]. The subjects of these investigations were optical absorption and luminescence of the DNA macromolecule. While absorption of the DNA and corresponding nucleotides has been thoroughly studied and results of these investigations are mainly well understood, the nature of the DNA fluorescence and phosphorescence is not sufficiently clear. The lack of more essential interest in the DNA emission can be partly explained by the fact that the quantum yield of the DNA fluorescence at room temperature is rather low ( $\sim 10^{-5}$ ) [11–14] and the DNA manifests phosphorescence only at low temperatures, well below the physiological range. As a result, there is a gap in the knowledge of the DNA energy structure and that of the processes following the electronic excitation of the  $\pi$ -electron systems of the DNA bases.

In the last years, a number of works appeared devoted to DNA photophysics, using spectroscopic methods [15, 16, 17, 18], as well as numerical simulations [19]. Particularly, time-resolved spectroscopic study of nucleotide bases led authors of [15] to the conclusion, that namely the extremely low fluorescence lifetime of the mentioned bases is responsible for the DNA self-protection against the photodamage. Formation of excimers between the nucleotide bases in DNA was revealed in [18]. The results of computer simulation of DNA energy structure [19] argued for the delocalization of electronic excitation in DNA for several nucleotide bases, according to the exciton model.

Nevertheless, though the ultra fast excitation relaxation of the separate nucleotides is important for the DNA self-protection against the photodamage, it remains still unclear whether the mentioned self-protection is only due to the individual nucleotide properties, or the mechanism of “safe” excitation deactivation involves energy transfer to other nucleotides of the DNA, being thus the collective mechanism. Since the excitation energy transfer processes depend on position of energy levels, the question can be put wider, namely whether the singlet and triplet levels of the adenine, thymine, guanine and cytosine nucleotide bases are arranged in a way that is not random but obeys an unrecognized hierarchy that affects the physical and chemical processes occurring with the DNA in the living systems, such as, for example, the DNA damage and/or aging.

In this paper, we describe our studies on the structure of the DNA triplet electronic energy levels, electronic excitation energy transfer along the triplet levels, and their relation to the DNA damage. Among the aims of the presented investigation was to identify the possible mechanisms of self-protection of the DNA macromolecule. The existence of such mechanisms that protect the DNA against different types of damage seems logical in view of the well-known stability of its structure. It is known that the high-energy ionization radiation absorbed by organic or inorganic substances, relaxes mainly to the electronic excitations of molecules and atoms [20]. Since similar electronic excitations can be also produced with UV-irradiation, there is a possibility to carry out experiments with UV irradiation that imitate the processes caused by the ionization radiation. We used this approach to find out if there is any mechanism of the DNA protection against photoreactions. The question can be put in a more general case, namely whether the reactions that are initiated by electronic excitation of the DNA (which appears, for example, in radiation field) are inhibited due to a peculiar arrangement of energy levels.

### Experimental

The total DNA from chicken erythrocytes and poly(dAdT)<sub>2</sub> polynucleotide were purchased from Sigma. The DNA was additionally purified with phenol.

The model compounds 5'-deoxyadenosinemonophosphate (dAMP), 5'-deoxythymidinemonophosphate (dTMP), 5'-deoxyguanosinemonophosphate dGMP, and 5'-deoxycytidinemonophosphate (dCMP) were obtained from the Institute of Molecular Biology and Genetics (IMBG) of the National Academy of Science of Ukraine. We believe that these compounds (contrary to rAMP, rGMP and rCMP that were used in [9]) can serve as a more exact model of the DNA elementary links. The poly(dAdT)<sub>2</sub> and d(ATC) obtained from IMBG were also used.

The model compounds 5'-CCCGGGTTTAAA-3', 5'-CCCCCCCCCCC-3', 5'-GGGGGGGGGGG G-3', 5'-TTTTTTTTTTTTT-3' and 5'-AAAAAAA AAAA-3' were synthesized in SUNY at Buffalo.

Samples were prepared in distilled water and 0.05 M TRIS-HCl buffer, pH 7.5. For the low-temperature measurements, the prepared solutions were poured out into the special cell so that the upper surface is open, and then frozen. The excitation beam was directed to the open surface, and from the same surface the luminescence was registered.

The steady state fluorescence measurements were performed with Hitachi 850 and MPF-4 spectrofluorometers; absorption spectra were recorded with the help of a Specord UV-VIS spectrophotometer. The phosphorescence spectra were obtained using laboratory-designed equipment.

The photodamage of the DNA and model compounds was performed by exposition of the corresponding solution (in quartz cell) to the full-spectrum irradiation of the 1 kW Hg-lamp. One of the most powerful lines in the Hg-lamp emission spectrum (at 254 nm) falls near the maximum of the absorption spectrum of the DNA and model compounds.

The measurements were carried out at 4.2 K, 77 K and ambient temperatures.

## Results and Discussion

### 1. DNA electronic energy levels structure: separate nucleotides or collective exciton levels?

The most crucial question in regarding the structure of DNA electronic energy levels is, whether the nucleotides in DNA absorb photons as separate absorbing centers, or the electronic states of nucleotides form the exciton states due to the interaction, the excitation being thus delocalized over the several nucleotides. In the works [21, 22] the experimental comparison of DNA absorption spectrum with the linear combination of nucleotides spectra was performed. Despite of the significant hypochromic effect observed for the DNA spectrum, the spectral shapes of the compared spectra are close and the shift of the spectrum maximum was negligibly small as compared to the absorption band half-width. This means that the nucleotides are practically independent absorbing centers in the DNA macromolecule and electronic processes in it start from initially excited DNA bases, similarly as it takes place for the synthetic aromatic-containing nonconjugated macromolecules [23–29]. It gives also a ground for the statement that the system of the electronic levels of the DNA may be compiled from the electronic levels of the corresponding nucleotides.

Nevertheless, in the works dealing with the theoretic calculations [6, 30] and computer simulations [19], the DNA energy states structure is treated in terms of exciton theory, regarding the DNA electronic energy states to be collective and excitations being delocalized over the several DNA nucleotides. We should mention that in principle for every ordered system of interacting monomers one can theoretically obtain the splitting of energy levels and exciton zone formation. But the most principal question is, whether such result really corre-

sponds to the description of the electronic processes in this system. In the work [31] describing the spectral manifestation of molecular aggregates, the three cases, namely these of strong, weak and very weak interaction, are regarded. While for the first two cases one can regard the collective excitation and exciton zone, the third one corresponds to the case of the excitation jumps between the separate monomers. For the case of very weak interaction, the spectral shift of the ordered system (polymer or aggregate) absorption spectrum relatively to the monomer one is much less than the monomer bandwidth, though the hypochromic effect could be observed. That is namely the case of the DNA, where no spectral shift of the DNA absorption spectrum as compared to the linear combination of the nucleotides is observed, but the strong hypochromic effect takes place. Thus there is no doubt that the interaction between p-electron systems of the nucleotides in DNA exists, and possibly it influences the position of the electronic energy levels of nucleotides, but this interaction is not enough for the formation of the exciton bands and collectivization of electronic excitations. It should be also mentioned, that for cyanine dyes intercalating into DNA some long-wavelength shift and hypochromism of the absorption spectrum is observed [32], though it is obvious that no exciton band could be formed by dye and nucleotide excited states, because of drastic difference in excitation energies.

Since the all above-mentioned conclusions were derived from the absorption spectra characteristics, they concern the singlet excited levels of the nucleotides. It should be noted, that unlike the singlet-singlet transitions, for the singlet-triplet ones the dipole transition moment is near to zero, thus the dipole-dipole interactions cannot be responsible for the possible electronic energy transfer (and thus for the formation of the exciton zone) [33]. The electronic excitation transfer between the triplet energy levels is only possible due to the exchange interactions, while between the singlet levels – due to the both dipole-dipole and exchange mechanisms. Thus the interactions between the nucleotides that could be responsible for the possible formation of exciton zone by triplet levels are much weaker than these responsible for the possible formation of exciton zone by singlet levels. The studies of molecular aggregates show that even when for the singlet excited states the exciton zone is formed, the triplet ones change insignificantly [34]. Thus, if in the case of DNA the singlet electronic energy levels of nucleotides could be regarded as practically independent (though influenced by

interaction with neighbor nucleotides), the triplet levels can be regarded as independent as well.

Hence, the triplet electronic energy levels system of DNA consists of the triplet levels of separate nucleotides. Though the interaction between the nucleotides in the DNA could influence the positions of the energy levels, the first step to study the DNA triplet levels system is to study the triplet levels of the separate nucleotides.

## 2. First excited triplet electronic energy levels of nucleotides

The DNA shows phosphorescence emission mainly at low temperatures. Only a few investigations [1, 4, 5, 7, 8–10] carried out in the sixties were devoted to the DNA phosphorescence because the main attention was concentrated on the room temperature studies. In [35] the measurements of quantum yields and phosphorescence lifetime of nucleic acids and the DNA components at 77 K were reported. Namely the phosphorescence spectra give the possibility to evaluate the position of the triplet levels of the DNA bases. These levels play an important role in processes caused by the appearance of the excitation in the macromolecule due to photon absorption or another action. But it should be noticed that in the above-mentioned works the study of DNA and nucleotides phosphorescence was performed in either ethylenglycol-water solution or in ethanol, that is different from the purely water medium and could influence the levels positions.

All of the phosphorescence spectra of dAMP, dTMP, dGMP and dCMP (models of the DNA bases) in water medium at 77 K and 4.2 K are in the range of 350–550 nm [41,44]. Phosphorescence spectra of dAMP and dGMP are more structured and more intense; dCMP and dTMP manifest weak phosphorescence with practically unstructured spectra. The spectra obtained at 77 K look similar to those obtained in [10, 35]. Change from 77 to 4.2 K leads to increasing of the phosphorescence intensity and structuring of the spectra. The blue edge of the spectra becomes sharper.

The position of blue edge of the phosphorescence spectra allows estimation of the position of triplet energy electronic levels (0-0 transition). While the blue edges of dCMP and dGMP can be determined quite definitely, the difference between dAMP and dTMP blue edges is not so clear at 77 K. At the first sight it seems that blue edge of phosphorescence spectrum of dTMP is red-shifted compared with phosphorescence edge of dAMP as it was concluded in [9]. But careful examination of the phosphorescence spectra at 77 K and data

obtained at 4.2 K [44] gives the ground to a conclusion that actually blue edge of dAMP is red shifted compared to the dTMP edge. The positions of the triplet levels determined from blue edges of dAMP, dTMP, dGMP and dCMP are given in Tabl.1 and Fig.1. Though in the DNA the level positions of nucleotides could be changed due to the interaction between nucleotides, we can suppose that the hierarchy of the triplet levels stays generally unchanged.

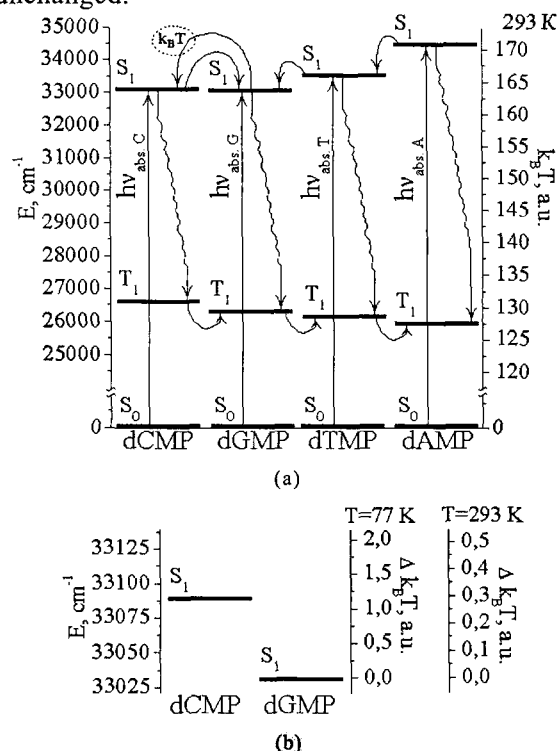


Fig. 1. The energy levels and scheme of triplet electronic excitation energy transfer in the DNA at  $T = 77$  K (a); the detailed layout of dCMP and dGMP singlet levels (b) in units of  $kT$  for 77 K and 293 K

From spectra and data presented in tabl.1 it follows that there are some red shifts of triplet level positions with the temperature increasing from 4.2 to 77 K. For dTMP and dAMP these shifts are  $\sim 140$   $\text{cm}^{-1}$  and  $170$   $\text{cm}^{-1}$ , the signs of temperature shifts being the same. Thus, we consider that this tendency will take place up to room temperature and that is the ground of our suggestion that the triplet level of the DNA adenine-base is situated lower than thymidine-base triplet level also at room temperature.

Table 1. Positions of triplet ( $T_1$ ) levels,  $\text{cm}^{-1}$  (Phosphorescence blue edge)

Compound	dCMP	dGMP	dTMP	dAMP
$T = 4.2$ K	27120	26400	26360	26120
$T = 77$ K	26630	26320	26160	25950

The values of triplet energy levels obtained in [9] are presented in Tabl.2. The differences

Table 2. Triplet energy levels (T) obtained from phosphorescence spectra blue edges,  $10^3 \text{ cm}^{-1}$  at pH 7 [9]

	rAMP	rGMP	rCMP	dTMP	rUMP
T	26.7	27.2	27.9	26.3	pH 12 28.4

between values of energy levels (except in the case of dTMP) obtained by us and in [9] can be explained by the fact that in our experiments deoxyribonucleotide were used in contrast to [9, 35] where ribonucleotide were used (the exception was dTMP for which the difference between values of corresponding energy levels was the smallest because the same compound was used in our experiments and those in [9]). Besides, in [9] ethylene-glycol solution was used, that is unlike the water solution used in our work.

### 3. Triplet excitation energy transfer in the DNA. The nature of the DNA phosphorescence

The behavior of triplet excitations in the DNA is the subject of special interest because this type of excitation should be responsible for the initiation of chemical reactions [36], which lead to undesired modification or destruction of the macromolecule.

In fig. 1 the system of the triplet electronic levels of the DNA bases is presented. The values of the energy for triplet levels decrease in the direction:  $C > G > T > A$ . It is clear that such positioning of the energy levels should lead to triplet excitation energy transfer to the A base in the DNA macromolecule (Fig. 1) although the spatial location of the bases in the DNA macromolecule in general is practically random.

Possibly, the intramolecular triplet excitation energy transfer was observed first on the DNA macromolecule by Berson and Isenberg in 1964. They studied the DNA phosphorescence and quenching of it by traps, due to  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ -ions [1]. The authors used the model of one-dimensional diffusion to describe the process of triplet excitations spreading in the DNA macromolecule. The average value of the triplet excitations spreading length was obtained to be close to 20 base pairs along the DNA chain. There were no other experimental works of such type up to now, though there were some papers that prove directly [37] or indirectly [38] the existence of the triplet excitation energy transfer in the DNA.

The triplet energy transfer along the DNA macromolecule should lead to localization of the migrating triplet excitations on the DNA bases with lowest triplet energy levels. As it was shown above, the triplet level of A base is the lowest. So, it seemed that the phosphorescence spectrum of the DNA

must be close to dAMP phosphorescence spectrum. But this is not the case. The DNA phosphorescence spectrum (Fig. 2) does not look like any of the bases phosphorescence spectra. In [10] it was supposed that the DNA phosphorescence spectrum is originated from ionized T base  $\pi$ -electron system. Our supposition is that at the beginning of the processes, the localization of the triplet excitations on the adenine groups takes place and then a triplet exciplex or another complex forms between adenine and neighbor base.

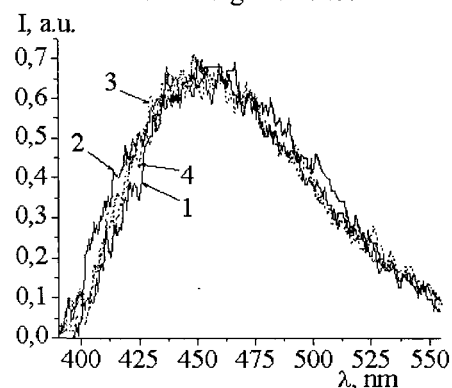


Fig. 2. Phosphorescence spectra of water solutions of (1) DNA, (2) poly(dAdT)<sub>2</sub>, (3) 5'CCCGGGTTTAAA3' and (4) d(ATC) at 77 K. Water solutions,  $C = 10^{-4} \text{ M}$ , excitation 300 nm

To check the proposed above pathway of the triplet excitation transfer along the DNA-macromolecule as well as positions of energy levels of the DNA bases and the origin of the DNA phosphorescence emission centers, the special oligomer compound 5'-CCCGGGTTTAAA-3' was designed and synthesized. It has the required hierarchy of triplet levels (Fig. 3).

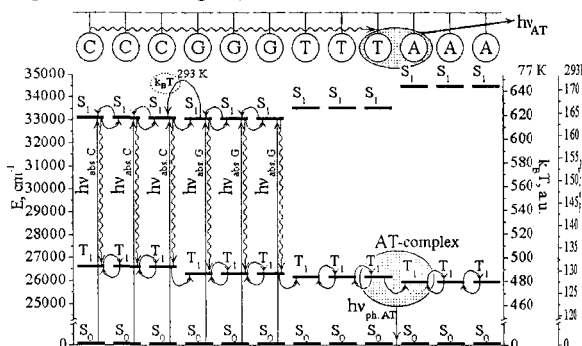


Fig. 3. The scheme of the energy sites and photophysical processes in 5'CCCGGGTTTAAA3' molecule

We also used poly(dAdT)<sub>2</sub> and specially designed oligomer compounds 5'-CCCCCCCCCCCC-3', 5'-GGGGGGGGGGGG-3', 5'-TTTTTTTTTTTT-3' and 5'-AAAAAAAAAAAA-3' (also 12 base length as is the case for 5'-CCCGGGTTTAAA-3'). Similar to the case of the DNA, the absorption spectrum of 5'-CCCGGGTTTAAA-3' is close to the sum of spectra of G,C,T,A-model compounds (dGMP, dCMP, dTMP and dAMP) spectra. It follows from the scheme of energy levels (Fig. 3) that

disposition of triplet levels in oligonucleotide 5'-CCCGGGTTTAAA-3' favors the triplet excitation energy transfer from CCC-links to AAA-links. It means that the excitation of this synthetic compound must result in phosphorescence of A-cells. But experiments show that triplet excitations are not deactivated from the A bases because there is a big difference between phosphorescence spectra of dAMP and the model oligomer. Besides, the phosphorescence spectrum of the oligomer does not correspond to the sum of dCMP, dGMP, dTMP and dAMP phosphorescence spectra, but it is very close to the DNA phosphorescence spectrum. The hypothesis that triplet excitations are localized in the excimer-like traps was checked using the 5'-CCC CCCCCCCC-3', 5'-GGGGGGGGGGGG-3', 5'-T TTTTTTTTTT-3' and 5'-AAAAAAAAAAAA-3'. The phosphorescence spectra of these compounds (Fig. 4) are rather different from phosphorescence spectra of 5'-CCCGGGTTTAAA-3' and the DNA (Fig. 2). It means that CCC, GGG, TTT and AAA-sequences in 5'-CCCGGGTTTAAA-3' oligomer molecule are not the trapping sites for the triplet excitations. But what is then? Probably, boundary pairs (between triads), e.g. AT, are joined in complexes (e.g. exciplexes sites) that can be the traps of triplet excitons.

Indeed, the investigations of poly(dAdT)<sub>2</sub> and d(ATC) luminescence have shown that the phosphorescence spectra of these compounds are very close to the 5'-CCCGGGTTTAAA-3' oligomer phosphorescence spectrum [44]. Moreover, the shapes of these three spectra are similar to the shape of the DNA phosphorescence spectrum (Fig. 2).

So, our conclusion is that intramolecular AT sequences in investigated model compounds as well as the AT sequences in the DNA are acting as traps for the triplet migrating excitations. The average value of the relative number of AT sequences in the chicken DNA, studied in this work, is about 1/16. It means that resulting average displacement of triplet excitons in the DNA equals to the distance that corresponds to sixteen base pairs length. This value is in agreement with Berson's and Isenberg's results (20 base pairs) [1].

It is well-known that triplet excited sites are often the centers where photochemical reactions originate. The results presented above prove that mobile triplet excitations in the DNA after the previous relaxation to A-bases are captured by traps formed in AT-sequences. So the photochemical reactions should start from A bases or AT sequences. However, it is worth noting that the triplet level of thymine base is very close to adenine triplet level

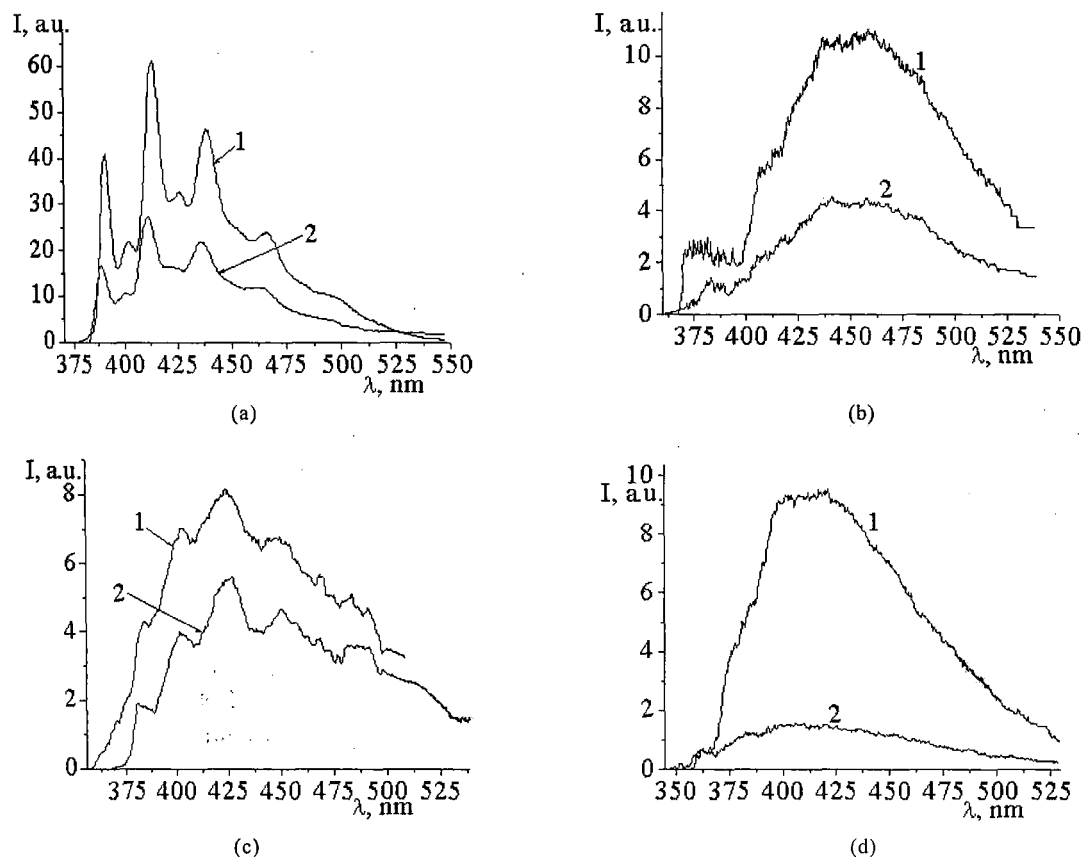


Fig. 4. Phosphorescence spectra of: (a) 5'-AAAAAAAAAAAA-3', (b) 5'-TTTTTTTTTTTT-3', (c) 5'-GGGGGGGGGGGG-3' and (d) 5'-CCCCCCCCCCCC-3' at 1 - T = 4,2 K, 2 - T = 77 K

(see the scheme above). Therefore, some light-induced or radiation-induced chemical reactions in the DNA can originate from T base triplet sites too. Additional information, in relation to specific photochemical reactions, is needed for more definite conclusions.

#### 4. UV-photodamage of DNA

The main aim of this part of work was to obtain the additional information on the identification of the sites of the triplet electronic excitation localization in the DNA using photochemical reactions and assuming that excited triplet sites favor these processes. The co-authors of this paper have some experience in spectral investigations of photochemical reactions in aromatic-containing synthetic macromolecules and using of the products of these reactions as traps for migrating excitations in macromolecules [25, 26, 28, 39]. Typical changes in the absorption spectra of these compounds upon UV or g-irradiation consist in the main absorption decrease and appearance of long wave absorption. For the DNA and model compounds investigated here these changes were to some extent different.

It is known that UV-irradiation destroys the DNA bases [38, 40, 41, 42, 44]. It becomes apparent in the decrease of the DNA absorption and some changes in the short-wave part of the DNA spectra (that prove the creation of the new absorption centers in the DNA identified as thymine dimers [42]). We have carried out the comparative investigations of the UV-damage of the DNA, model base compounds (dAMP, dTMP, dCMP, dGMP) and poly(dAdT)<sub>2</sub>. In fig. 5 the dependencies of the DNA and model compounds absorption at 260 nm on the time of UV-exposure are presented. As it follows from fig. 5 the initial decrease rate of absorption for dTMP, dCMP and dGMP (I) is essentially higher than for dAMP. This is in agreement with data obtained in [42, 43]. It is known

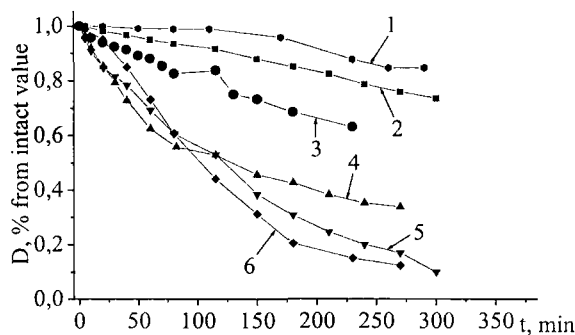


Fig. 5. The dependence of the optical density in the absorption maxima of: 1 - poly(dAdT)<sub>2</sub>, 2 - dAMP, 3 - DNA, 4 - dCMP, 5 - dTMP and 6 - dGMP on the time of UV-irradiation. T = 293 K. Water solutions, C = 10<sup>-4</sup> M

that adenine base in the DNA is the most stable relative to other bases [43]. According to our data (Fig. 5) the rates of decrease in the absorption of the DNA and dAMP under UV-irradiation are close. It proves our suggestion that the main part of triplet excitations are initially localized on the adenine bases. On the other hand, the phosphorescence data shows the localization of the mobile triplet excitations on the AT-base sequences. In this case, the localization of the triplet excitations in the AT-sequences must lead to the similar initial damage rate for the DNA and poly(dAdT)<sub>2</sub>. Indeed, the rate of the change in absorbance of the DNA upon UV-irradiation is closer to the rate of the corresponding change for dAMP and poly(dAdT)<sub>2</sub> [44, 45].

Slightly faster changes for DNA compared with dAMP and poly(dAdT)<sub>2</sub>, in our opinion, are connected with the localization of some part of triplet excitations on the other DNA-bases (e. g. on TT sequence producing T-dimers [38, 42]) for which UV-induced damage rate is essentially higher [41, 42].

It appears that the system of the DNA electronic levels is organized in such a way (Fig.1) that the processes of the electronic excitation energy transfer favor localizing of triplet excitations on the adenine groups or AT-complexes that are the most stable [41, 43-45].

#### Conclusions

As follows from results described above, the lowest excited triplet electronic level is connected with adenine bases. The comparative studies of the DNA and the model compounds show that AT sequences are main triplet traps for the native DNA, and the nature of the DNA phosphorescence is mainly determined by these AT-sequences. The mobile triplet excitations in the DNA can spread on the distance of about 16 base pairs. It is known that singlet electronic excitations are short living (particularly in the DNA). That is why the points of the localization of the singlet excitations are not suitable for initiation of the chemical reactions. The reactions that cause the DNA-bases damage (due to the electronic excitation energy transfer and capture of triplet excitations) occur most probably in the centers of triplet excitations localization. At least in the first stage of the UV-irradiation of the DNA, the rate of the DNA damage is close to that for the damage of the adenine base model compound as well as poly(dAdT)<sub>2</sub>. This additionally testifies to that A bases and mostly AT sequences are indeed the sites for localization of triplet excitons in the DNA. Of course, it is worth to stress that the excited triplet level of the thymine base is

near the adenine triplet level and the difference between their energy values  $\Delta E \sim kT$  (at 293 K). That is why the part of thymine triplet excited sites can initiate some chemical reactions before the triplet excitation transfer to adenine bases and following excitation localization on AT-sequences. Nevertheless, the main part of the triplet excitations in the DNA are localized on the traps associated with AT-sequences, that are photostable.

Finally, we would like to conclude that the mechanism of the DNA self-protection against damage of  $\pi$ -electronic systems of this macromolecule (caused by their excitations of different origins) exists. The positions of the DNA bases electronic levels are not random. This hierarchy favors the electronic excitation energy transfer to photostable centers in the DNA that leads to inhibition of photochemical damage of the DNA.

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## **ВПЛИВ ТРИПЛЕТ-ТРИПЛЕТНОГО ПЕРЕНОСЕННЯ ЕНЕРГІЇ ЕЛЕКТРОННОГО ЗБУДЖЕННЯ НА МЕХАНІЗМ САМОЗАХИСТУ ДНК**

*За допомогою спектрів електронного поглинання та фосфоресценції було досліджено розташування енергетичних рівнів ДНК, перенесення енергії електронного збудження триплетними рівнями та його відношення до руйнування ДНК під дією УФ-випромінювання. Показано, що найнижчий збуджений триплетний електронний рівень ДНК (а також: і найвищий синглетний) належить аденіновій ланці. Однак основними пастками триплетних збуджень в ДНК є АТ-послідовності і фосфоресценція ДНК, пов'язана саме з цими пастками. Припускається, що мобільні триплетні збудження в ДНК можуть поширюватися на відстані, що дорівнюють довжині 16 базових пар нуклеотидів. Згідно з отриманими даними, переважна більшість триплетних збуджень у ДНК зрештою локалізується на фотостабільних пастках, пов'язаних з АТ-послідовностями. Таким чином, ієрархія розташування електронних рівнів баз ДНК сприяє процесу перенесення енергії електронного збудження триплетними рівнями, що призводить до істотного стримування фотохімічного руйнування ДНК. Цей факт доведено дослідженнями, спричиненого УФ-випромінюванням фоторуйнування ДНК та модельних базових сполук. Останнє доводить існування механізму самозахисту ДНК проти руйнування π-електронних систем цієї макромолекули (спричиненого їх збудженням різного походження).*